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UV and Fluorescence Studies for Vinyl Polymerization

by

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13. ABSTRACT (Maximum 200 words)  Polymerizations of styrene and methyl methacrylate (MMA) in bulk as well as in solutions were followed by UV-Visible and fluorescence spectroscopies as potential on-line monitoring techniques. For the solution polymerization of styrene, the monomer conversion obtained by UV and fluorescence measurements could be correlated with IR results at three different temperatures: 65, 70, and 75°C. From the initial slope at each temperature, the activation energy of about 6Kcal/mol was determined. For MMA solution polymerization, UV of MMA and fluorescence of styrene laced as an extrinsic sensor were monitored. The monomer conversion of this reaction could be obtained by measuring fluorescence intensity of styrene through the correlation curve. Bulk polymerization of styrene was in-situ monitored by using fluorescence fiber-optic cable. The fluorescence intensity of styrene in bulk became significant only after 80% monomer conversion because of self-quenching effect. Bulk polymerization of MMA was followed by UV reflection technique. The initial peak appeared at 225 nm was gradually shifted to the shorter wavelength with polymerization, which is not observable in UV transmission absorption spectra. Also, the percent reflectance increased with reaction. Based on these results, this technique showed a promising future as an on-line monitoring tool.					
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## UV and Fluorescence Studies for Vinyl Polymerization

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### INTRODUCTION

Recently, there has been a considerable effort in the area of on-line measurements and control of polymerization reactors (1). The main goals of on-line monitoring techniques are high yield, high product quality and safe operation in operating a polymer reactor. Although there are several techniques developed for this purpose as reviewed in recent papers (1,2), each method has limitations in some aspects.

Several fluorescence studies using viscosity sensitive, extrinsic probes to follow vinyl polymerization have been reported (3, 4). The fluorescence response of these probes is not sensitive until the monomer conversion reaches more than 50%. In some monomers such as styrene and MMA, double bond in vinyl group is in conjugation with the side group. Upon polymerization, the conjugated double bond disappears, causing great changes in UV and/or fluorescence spectra. Therefore, it may be advantageous to use an intrinsic fluorescent monomer if its response is more sensitive to the conversion. In case where a monomer is not fluorescent, one can use a small amount of fluorescent comonomer with a similar reactivity as an extrinsic sensor. In this study, we investigate the polymerizations of styrene and methyl methacrylate (MMA) in bulk as well as in solution using UV-visible and fluorescence spectroscopies. For polymerization of styrene, UV and fluorescence of styrene are monitored. For MMA polymerization, UV of MMA and fluorescence of a small amount of styrene are monitored. Especially, UV reflection and fiber-optic fluorescence cable were employed for the bulk polymerizations as potential on-line monitoring techniques.

### EXPERIMENTAL

Vacuum distilled monomer (styrene or MMA) and polymer (PS and PMMA) after several precipitation were used for the measurements of extinction coefficients using Perkin-Elmer Diode-Array UV-Visible spectrophotometer (Model 3840) and fluorescence intensity using Perkin-Elmer fluorometer (MPF-66). The excitation wavelength was set at 255 nm for styrene and polystyrene. 1,2-dichloroethane was used as a solvent. Monomer concentrations for solution polymerizations were about 10% by weight and benzoyl peroxide (BPO) was used as an initiator. For the case of styrene, the reaction was undertaken under the purge of argon gas at three different temperatures: 65°C, 70°C and 75°C, whereas only one temperature, 75°C, was studied for MMA. For the UV and fluorescence measurements, an aliquot (50  $\mu$ l) was taken at a certain time interval and then diluted for measurements. For the styrene case, the same sample was used for both UV and fluorescence measurements by exciting at 280 nm. Solution polymerization of MMA was studied in two different ways: pure MMA system and MMA laced with styrene (0.1%) as an extrinsic reactive sensor. The solution was excited at 250 nm to obtain the emission spectrum of styrene. Monomer conversion was also followed by FT-IR to compare with the results obtained by UV and fluorescence spectroscopies.

Monitoring of bulk polymerizations of styrene and methyl methacrylate were carried by a fiber-optic fluorescence cable (Model LS 50) and UV reflection (Model Lambda 6), respectively. For the styrene case, 2% of BPO was used as an initiator. The reaction temperature was 130°C for initial 6 hours, followed by heating at 180°C for about 33 hours. Independent study for the extent of reaction was performed by FT-IR. The sample was excited at 250 nm and 300 nm. For the

bulk polymerization of MMA, 0.1% of BPO was used as an initiator. The reaction was undertaken in the oven at 75°C for 560 minutes. The sample holder was placed on the UV-reflection tip in such a way that the analyzing light always hit the same sample position. The extent of reaction was obtained by FT-IR study.

### RESULTS AND DISCUSSION

From the study of characteristics of UV and fluorescence spectra of styrene and polystyrene, it was found that the extinction coefficient of styrene at 250 nm is about 100 times greater than that of polystyrene and the fluorescence intensity of styrene is about 550 times greater than that of polystyrene. The spectral shift due to the reduced conjugation with opening double bond of monomer was not observable simply because of the large difference in extinction coefficient. Using these characteristics, polymerization of styrene can be easily followed. Figures 1-(a) and 1-(b) show the change of UV-visible and fluorescence spectra with polymerization of styrene in solution at 75°C. The absorption peak at 250 nm and the fluorescence emission peak at 308 nm were decreasing with reaction. The monomer conversions obtained by these techniques were compared with that obtained by FT-IR. The monomer conversions of solution polymerization of styrene at three different temperatures were summarized in Figure 2. It shows that there is a good agreement among the results obtained by three different techniques at each temperature. Using the initial slope at each temperature, the activation energy of about 6 Kcal/mol was determined. Figure 3 shows the correlation between UV or fluorescence result and IR result of the solution polymerization of styrene at 75°C. From this relationship, % monomer conversion at any time during the reaction can be obtained by measuring the normalized absorbance or fluorescence intensity. Similar results were obtained for other temperatures.

Solution polymerization of MMA laced with a small amount of styrene (0.1%) was followed by UV and IR spectroscopies monitoring MMA disappearance as well as by fluorescence spectroscopy monitoring styrene disappearance. As shown in Figure 4, styrene was consumed much faster than MMA even though the monomer reactivity ratios of these monomers are close ( $r_{\text{MMA}} = 0.46$  and  $r_{\text{styrene}} = 0.52$ ). However, it was confirmed that this result is reasonable by considering the instantaneous copolymer composition as a function of conversion. Although both UV and IR spectroscopies monitored MMA disappearance, there was a significant discrepancy between these results. This was ascribed to the underestimation of UV result due to the interference of solvent. The % MMA conversion, however, can be obtained by measuring fluorescence intensity of styrene through the correlation curve between the change in the fluorescence intensity of styrene and the % conversion of MMA as shown in Figure 5.

Bulk polymerization of styrene was in-situ monitored by a fluorescence fiber-optic cable. It was found that the fluorescence of styrene in bulk polymerization became rather significant only after about 80% monomer conversion because of self-quenching.

Bulk polymerization of MMA was followed by UV reflection technique. Figure 6 shows the change of the UV reflection spectra of MMA with polymerization at 75°C. Although, the UV absorption spectrum of MMA in solution has interference from the solvent, the UV reflection spectrum of MMA in bulk was obtained without any interference. Due to the characteristics of UV reflection technique which causes a spectral shift to the longer wavelength, the initial peak position appears at 225 nm. It was gradually shifted to the shorter wavelength and the percent reflection (%R) at the peak maximum increased with polymerization. These changes can be correlated with monomer conversion. From this study, a couple of points should be noted. First of all, it is possible to

follow the reaction of MMA by monitoring spectral shift of UV reflection spectra, which is not feasible with UV transmission absorption spectra. Secondary, a thick film which is out of scale in UV absorbance can be investigated with UV reflection technique due to the limited depth of penetration of light. This is an important feature from a practical viewpoint. The development of this technique is still in progress in our group.

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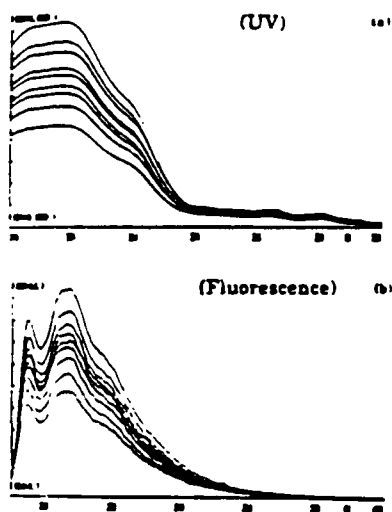


Figure 1. Changes of UV-visible and emission spectra of styrene with polymerization at 75°C. (reaction hours: 0, 1, 2, 3, 4, 6, 8, 12, 22, from top to bottom)

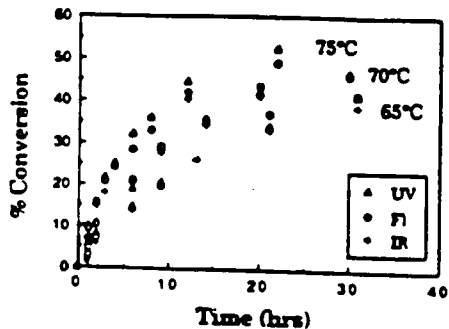


Figure 2. % monomer conversion of styrene polymerization at three different temperatures by UV, fluorescence and IR spectroscopies

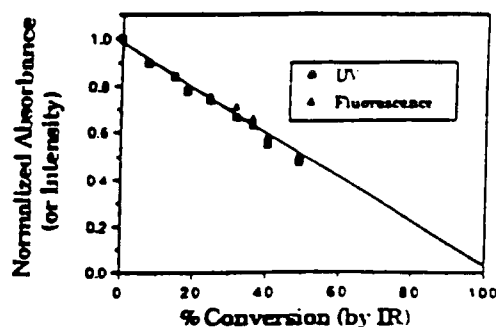


Figure 3. Correlation between UV or fluorescence and IR measurements of solution polymerization of styrene at 75°C

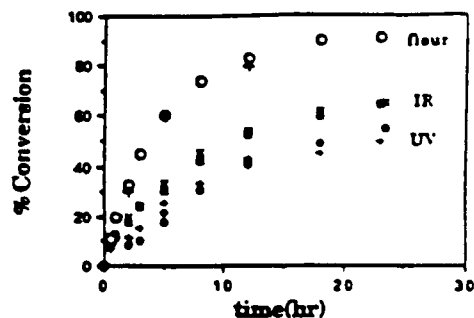


Figure 4. Correlation among the measurements of UV (MMA), of the fluorescence (styrene) and of the IR (MMA)

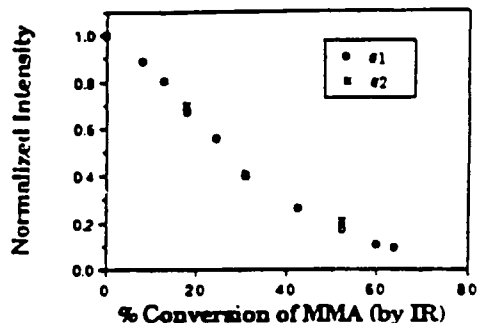


Figure 5. Correlation between fluorescence (styrene) and IR (MMA) results of solution polymerization of MMA at 75°C

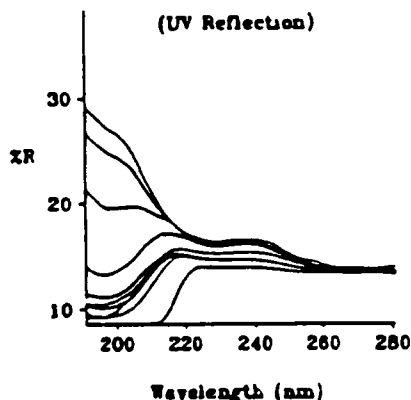


Figure 6. UV reflection spectra of MMA with polymerization at 75°C (0.1% BPO) (time (min): 660, 640, 320, 300, 300, 140, 60, 30, 10, 0, from left to right)

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